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GALLIUM NITRIDE OPTOELECTRONIC DEVICES

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Final Technical Report

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by

Ting L. Chu and Shirley S. Chu

Electronic Sciences Center

Southern Methodist University

Dallas, Texas 75222

for

Langley Research Center

National Aeronautics and Space Administration

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Summary

The objectives of this program are to investigate the crystal growth of gallium nitride in the form of bulk crystals and epitaxial layers, to characterize their structural and electrical properties, and to fabricate gallium nitride p-n junctions for optoelectronic devices.

Five approaches have been explored for the growth of bulk gallium nitride crystals: the closed-tube chemical transport, recrystallization from a gallium solution, sublimation of gallium nitride or gallium trioxide in an ammonia atmosphere, ammonolysis of gallium suboxide, and ammonolysis of gallium monochloride. Extensive investigations have shown that the ammonolysis of gallium monochloride is the best approach, producing gallium nitride single crystals up to $2.5 \times 1.0 \times 0.5$ cm in size, heretofore unknown. The single crystallinity of these crystals was verified by the chemical etching and optical microscopy and x-ray diffraction techniques. These crystals, with an electron concentration of 10^{19} cm^{-3} and Hall mobilities in the range of $100-160 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at room temperature, are suitable as substrates for the epitaxial growth of gallium nitride.

The epitaxial growth of gallium nitride on sapphire substrates with main faces of (0001) and (1102) orientations has been achieved by the ammonolysis of gallium monochloride in a gas flow system. The important parameters of this process, such as the geometry of the growth apparatus, the composition and flow rates of the reactants, and the substrate temperature, have been studies in detail. The grown layers had electron concentrations in the range of $1-3 \times 10^{19} \text{ cm}^{-3}$ and Hall mobilities in the range of $50-100 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at room temperature.

I. Introduction

This is the final technical report of a research program on the gallium nitride optoelectronic devices sponsored by the Langley Research Center of the National Aeronautics and Space Administration, Hampton, Virginia. The objectives of this program are to investigate the crystal growth of gallium nitride, to characterize the structural and electrical properties of gallium nitride crystals, and to fabricate gallium nitride p-n junctions for optoelectronic devices.

Gallium nitride is a direct gap semiconductor with a room temperature energy gap of about 3.4 eV.⁽¹⁾ This material is well-suited for the fabrication of lasers and light-emitting devices operating in the near-ultraviolet and visible regions of the spectrum. Stimulated emission and laser action have been observed at 2°K from optically pumped single-crystal needles of n-type gallium nitride ($n \geq 10^{19} \text{ cm}^{-3}$ at 300°K) at 3.45 eV.⁽²⁾ Green dc electroluminescence has been observed at room temperature from gallium nitride diodes of the (n-zinc doped insulator) configuration.⁽³⁾ However, the further development of these applications is hindered by the difficulties encountered in the growth of gallium nitride single crystals of good structural perfection and controlled distribution of shallow dopants.

Gallium nitride crystallizes in the wurtzite structure with lattice parameters $a = 3.18 \text{ \AA}$ and $c = 5.16 \text{ \AA}$. It undergoes thermal dissociation into gallium and nitrogen. The equilibrium vapor pressure of gallium nitride measured by the torsion-Langmuir method in the temperature range 1160° - 1430°K can be expressed by the relation:⁽⁴⁾

$$\log P_{\text{atm}} = 5.699 - 15,923/T$$

Thus, its vapor pressures are approximately 2.7×10^{-8} and 2.1×10^{-6} atm. at 1200° and 1400°K, respectively. Gallium nitride has been reported to

undergo dissociation at temperatures as low as 600°C.⁽⁵⁾ This thermal instability has prohibited the use of the melt techniques for the crystal growth of gallium nitride. Furthermore, gallium nitride crystals prepared by other techniques at high temperatures tend to be nitrogen-deficient, and the nitrogen vacancies behave as donors, contributing to the electrical conductivity.

Thus far, gallium nitride crystals have only been grown by vapor growth techniques using evaporation and chemical deposition. Epitaxial gallium nitride layers have been grown on the basal plane of sapphire and the {111} surface of gallium arsenide at 550°C by the evaporation of gallium in a nitrogen discharge.⁽⁶⁾ Layers prepared in this manner were of low-resistivity n-type due presumably to the presence of nitrogen vacancies. The chemical deposition techniques are more flexible. The reaction between gallium monochloride and ammonia in a hydrogen atmosphere has produced epitaxial layers of gallium nitride on the basal plane of sapphire at 825°C.⁽⁷⁾ However, the crystals grown with no intentional doping have a high inherent electron concentration, 10^{19} cm^{-3} , due to nitrogen vacancies. Later work on the ammonolysis of gallium monochloride indicated that the use of a helium or nitrogen atmosphere instead of a hydrogen atmosphere could reduce considerably the concentration of nitrogen vacancies.^(8,9) Gallium nitride epitaxial layers with relative low concentration of nitrogen vacancies have also been produced by the thermal decomposition of a gallium tribromide-ammonia complex at 500 - 600°C.⁽¹⁰⁾ However, the epitaxial layers and crystals of gallium nitride grown to date have all been of n-type conductivity. Attempts of incorporating group IIB elements, such as zinc, into vapor grown gallium nitride have not been successful in producing p-type material; zinc, though a shallow acceptor in gallium arsenide and gallium phosphide, has a deep acceptor state in gallium nitride.⁽³⁾

Because of its thermal instability, vapor and solution growth techniques have been used to investigate the preparation of device quality gallium nitride. The solution growth technique was found to be unsuitable because of the low solubility of gallium nitride in gallium. Vapor growth techniques were studied in detail for the growth of gallium nitride in the form of bulk crystals and epitaxial layers. Large single crystals of gallium nitride, heretofore unknown, have been produced for the first time and characterized. This represents a major breakthrough in the gallium nitride technology. Epitaxial layers of gallium nitride have also been grown on sapphire and gallium nitride substrates, and their properties have been investigated. Homoepitaxial gallium nitride layers are structurally superior to gallium nitride layers grown on sapphire substrates. These results are summarized in the following sections.

II. Technical Discussion

The technical approaches selected for this program were essentially the growth of bulk crystals and epitaxial layers of gallium nitride and to determine their electrical properties. Extensive investigations were carried out for the preparation and characterization of crystals and epitaxial layers of gallium nitride, and the results are discussed below.

II.A Growth of Gallium Nitride Crystals

Investigations on the preparation of gallium nitride crystals have been directed mostly to the heteroepitaxial growth on foreign substrates such as sapphire and silicon carbide.⁽⁶⁻¹⁰⁾ Because of the differences in the lattice parameters and thermal expansion coefficients of gallium nitride and the substrates, the grown layers have high concentrations of structural defects. Gallium nitride single crystals are the most ideal substrate for the epitaxial growth process, and considerable efforts have been devoted in this work to the growth of bulk gallium nitride crystals.

Because of the unfavorable thermodynamic properties, high melting point and high dissociation pressure, the growth of gallium nitride crystals is best carried out by vapor and solution growth techniques. The use of relatively low temperatures in these techniques will minimize the dissociation of gallium nitride. Five techniques have been investigated for the crystal growth of gallium nitride: the closed-tube chemical transport, recrystallization from solution, ammonolysis of gallium suboxide, sublimation, and ammonolysis of gallium monochloride.

II.A.1. Crystal Growth by Chemical Transport

The chemical transport in a closed tube has been used widely for the crystal growth of electronic materials. In this method, a solid reacts with a gaseous transport agent to form volatile products which, in turn, undergo the reverse reaction in a different temperature region of the system to

the reverse reaction in a different temperature region of the system to form the original material. Single crystals can be obtained by controlling the nucleation and growth processes in the deposition region. The choice of the transport agent is an important consideration. Since gallium nitride undergoes thermal dissociation at high temperatures and gallium reacts with ammonia to yield gallium nitride, ammonium chloride is expected to be a satisfactory reagent for the transport of gallium nitride.

The transport of gallium nitride was carried out in a fused silica tube of 25 mm ID and 29 mm OD. Polycrystalline gallium nitride, obtained by heating gallium trioxide at 900°C in an ammonia flow was used as the source material. In a typical experiment, a mixture of 1 g. gallium nitride and 0.08 g. ammonium chloride was placed in the reaction tube, evacuated to 10^{-5} Torr or less, and sealed. The reaction tube, approximately 30 cm in length after sealing, was placed in a horizontal tube furnace containing two independently controlled temperature zones. The region of the tube containing the source material was placed in the high-temperature zone, 900°C, and the lower temperature region of the tube was 100-200°C lower. There was a considerable amount of transport after about three days; however, the deposit was grayish in color due presumably to the partial decomposition of gallium nitride. Also the reaction tube exploded occasionally due to the pressure increase associated with the decomposition process. This transport process was not further explored.

II.A.2 Growth from Solution

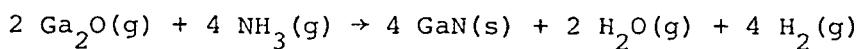
The solution growth technique has been widely used for the crystal growth of gallium phosphide and has greatly reduced the problems associated with its high dissociation pressure. This technique is based on the fact that solubility of gallium phosphide in gallium increases with increasing

temperature. The solubility of gallium phosphide in gallium is about 1 and 6 mole per cent at 1000° and 1100°C, respectively, and gallium phosphide platelets up to 1 cm² have been obtained by the slow cooling of a saturated solution at 1100-1125°C. ⁽¹¹⁾

To determine the feasibility of using the solution growth technique for the crystal growth of gallium nitride, experiments were carried out to estimate its solubility in gallium. A mixture of gallium and polycrystalline gallium nitride was sealed in a fused silica tube and heated at 700°C for three days. This tube was then slow cooled. Close examination of the resulting mixture indicated that gallium nitride is essentially insoluble in gallium at 700°C. Solubility determinations at higher temperatures must be carried out in the presence of ammonia to suppress the decomposition of gallium nitride. A mixture of gallium and gallium nitride was placed in a fused silica tube provided with gas inlet and exhaust tubes. The mixture was heated at 1100°C while ammonia was passed over the surface of the mixture at a rate of 100 ml/min. Since there were no indications of recrystallization of gallium nitride upon cooling, it is concluded that the solubility of gallium nitride in gallium is very low at 1100°C. No further experiments were carried out.

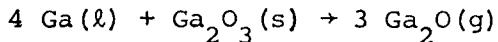
II.A.3. Growth by Ammonolysis of Gallium Suboxide

Gallium nitride can be prepared by the reaction of ammonia with a volatile gallium compound. Gallium suboxide, Ga₂O, has been reported to have an appreciate vapor pressure at temperatures below 1000°C ⁽¹²⁾ and is used in this work for the growth of gallium nitride crystals according to the reaction:



The suboxide was prepared by the reaction of gallium and gallium trioxide

according to the reaction:



Although gallium and gallium trioxide have very low vapor pressures at high temperatures, the equilibrium vapor pressure of gallium suboxide over a 4:1 molar mixture of gallium and gallium oxide is approximately 0.2 Torr at 800°C and 10 Torr at 1000°C.

The apparatus used for the growth of gallium nitride crystals by the ammonolysis of gallium suboxide is shown in Fig. 1. The formation of gallium suboxide took place in the quartz boat containing a mixture of gallium and gallium trioxide, and the nitrogen flow was used to carry the suboxide vapor into the reaction tube. The suboxide then reacted with the ammonia, which was introduced separately into the reaction zone. The experiments were carried out with the quartz boat in the temperature range 875°-1050°C and the reaction zone in the temperature range 1000°-1200°C. The flow rate of ammonia was 400 ml/min, and that of nitrogen through the quartz boat was 200-600 ml/min (the other nitrogen inlet was only used to purge the reaction tube prior to the heating of the furnace). The temperature of the quartz boat, or the suboxide formation temperature, was found to be not critical; however, gallium nitride crystals were obtained only for a reaction zone temperature of 1150° ± 10°C. Needle-like gallium nitride crystals dark green in color and up to 1 mm in size, were found near the ammonia outlet. Dendritic crystals with dimensions up to 3 mm were sometimes found also. The efficiency of this technique under the conditions used here is limited by the vaporization from the boat of free gallium which was found near the reaction zone.

II.A.3. Growth by Sublimation

Since gallium nitride undergoes thermal dissociation and the resulting gallium also has a measurable vapor pressure at temperatures above 1100°C, it is conceivable that the sublimation of gallium nitride in an ammonia

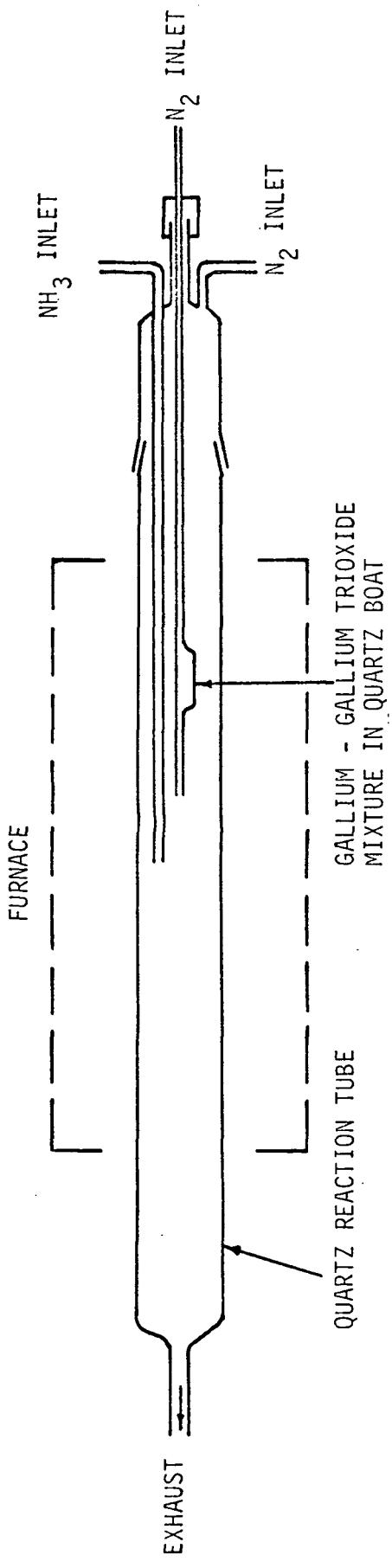


Fig. 1. Schematic diagram of the apparatus for the growth of gallium nitride crystals by the reaction of gallium suboxide with ammonia.

it is conceivable that the sublimation of gallium nitride in an ammonia atmosphere may be used for the crystal growth of gallium nitride. Gallium or gallium oxide may also be used as the starting material since they are converted into the nitride in the presence of ammonia at high temperatures.

The apparatus for the sublimation method consisted of a single zone furnace with a fused silica reaction tube. Provision was made to introduce ammonia or ammonia-containing gases at various flow rates and pressures. Six types of source material were used: (1) gallium trioxide powder, (2) gallium nitride powder, (3) a mixture of gallium and gallium trioxide, (4) a mixture of gallium and gallium nitride, (5) pressed pellets of gallium and gallium trioxide, and (6) pressed pellets of gallium and gallium nitride.

The initial experiments were carried out with loosely packed powder of gallium trioxide or gallium nitride in an alumnia boat using ammonia at a flow rate of 50 ml/min. A reaction temperature of 1170°C was found to be optimum, and experiments were carried out for different time periods. Typically after three days, very small crystals of gallium nitride were found in the boat. With a fifteen day growth period, crystals were found at two locations. Dark green, slightly transparent, n-type, needle-shaped crystals up to 3 mm long by 0.2 mm thick were found on the wall downstream from the source material; the dark color is due apparently to the thermal decomposition of gallium nitride. Transparent crystals of 0.4 x 0.04 mm dimensions were found in the boat. These results were not changed by using a mixture of 20% NH_3 and 80% N_2 as the carrier gas. In an attempt to suppress the decomposition of gallium nitride, a series of sublimation experiments were carried out under an ammonia pressure of 5 atm. The gallium oxide source material was placed in an alumina boat in a fused silica liner located in a ceramic reaction tube. The ceramic tube has appropriate fittings so that a

high ammonia pressure can be maintained with a controlled flow rate.

Typically, the source material was at 1170°C, the flow rate of ammonia was 50 ml/min and the pressure in the reaction tube was 5 atm. No improvements in the size of the gallium nitride crystals were observed. It was also observed that no crystals formed at reaction zone temperatures much below 1150°C or higher than about 1180°C.

Similar experiments were carried out with powdered mixtures of gallium-gallium trioxide and gallium-gallium nitride. There was a tendency for larger gallium nitride crystals to grow in the boat, and crystals were also formed downstream on the wall of the reaction tube. A third series of experiments was carried out with pressed pellets of gallium-gallium trioxide and gallium-gallium nitride mixtures. The pellets, approximately 1 g in weight, were made with a Parr 2811 pellet press capable of producing $\frac{1}{2}$ " diameter pellets at a pressure of approximately 5,000 lbs/in². They were placed in an alumnia boat located at the maximum temperature zone in the furnace liner. A source temperature of 1160° ± 10°C was found to be necessary for obtaining crystals of reasonable size, and the crystal growth experiments were carried out for periods of up to 20 days. Needle-like crystals up to 3 mm long by 0.5 mm thick were obtained in two locations. Light colored crystals were found growing inward from the surface of the pellets, and dark green crystals were found on the wall of the reaction tube downstream from the pellets. Usually one type or the other dominated in a particular experiment. The exact reason for this has not been established, and the composition of the pellet and the pressure used in its formation could be significant. The results were independent of the flow of ammonia in the range 200 to 800 ml/min. Figure 2 shows examples of the two types of gallium nitride crystals. These crystals were shown to be single

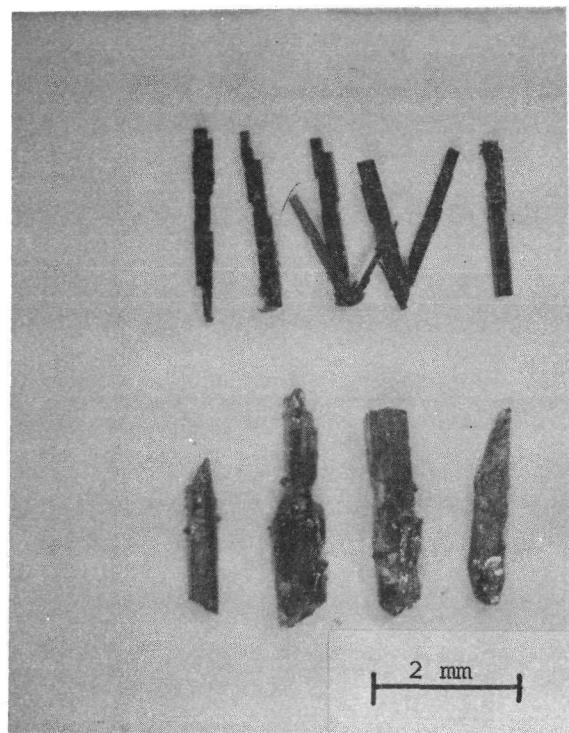
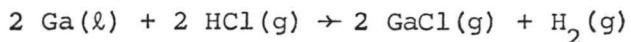


Fig. 2 Gallium nitride crystals grown on the wall of the silica tube (upper) and in the alumina boat (lower) by the sublimation technique.

crystalline by the x-ray diffractions technique. Chemical etching of these crystals with a 40% sodium hydroxide solutions for 30 min revealed no significant structural defects. The vapor grown crystals are always n-type with low electrical resistivities. Using indium as ohmic contacts, the electrical resistivities of these crystals were measured over a wide temperature range, and the typical results are shown in Fig. 3. The darker crystals have a lower resistivity than the light crystals as expected. The resistivity is essentially independent of temperature in the range 160°-330°K, indicating the presence of a high concentratior of shallow impurities, presumably nitrogen vacancies.

II.A5. Ammonolysis of Gallium Monochloride

A significant improvement in the size of gallium nitride crystals has been obtained by the ammonolysis of gallium monochloride. This process involves two steps: the formation of gallium monochloride by the reaction of gallium with hydrogen chloride, and the reaction of gallium monochloride with ammonia to form gallium nitride. The chemical reactions are:



The apparatus for this process is shown schematically in Fig 4. It consists of a fused silica reaction tube of 4.5 cm ID and 90 cm length situated in a two-zone resistance-heated furnace. The ends of the reaction tube are provided with standard taper joints. The end cap on the gas inlet side has provisions for introducing hydrogen chloride mixed with a diluent, helium or hydrogen, and for introducing ammonia to the reaction zone. Gallium was placed in an alumina boat and was heated by one of the heaters, and the rate of formation of gallium monochloride was determined mainly by the flow rate of hydrogen chloride. Single crystalline sapphire platelets

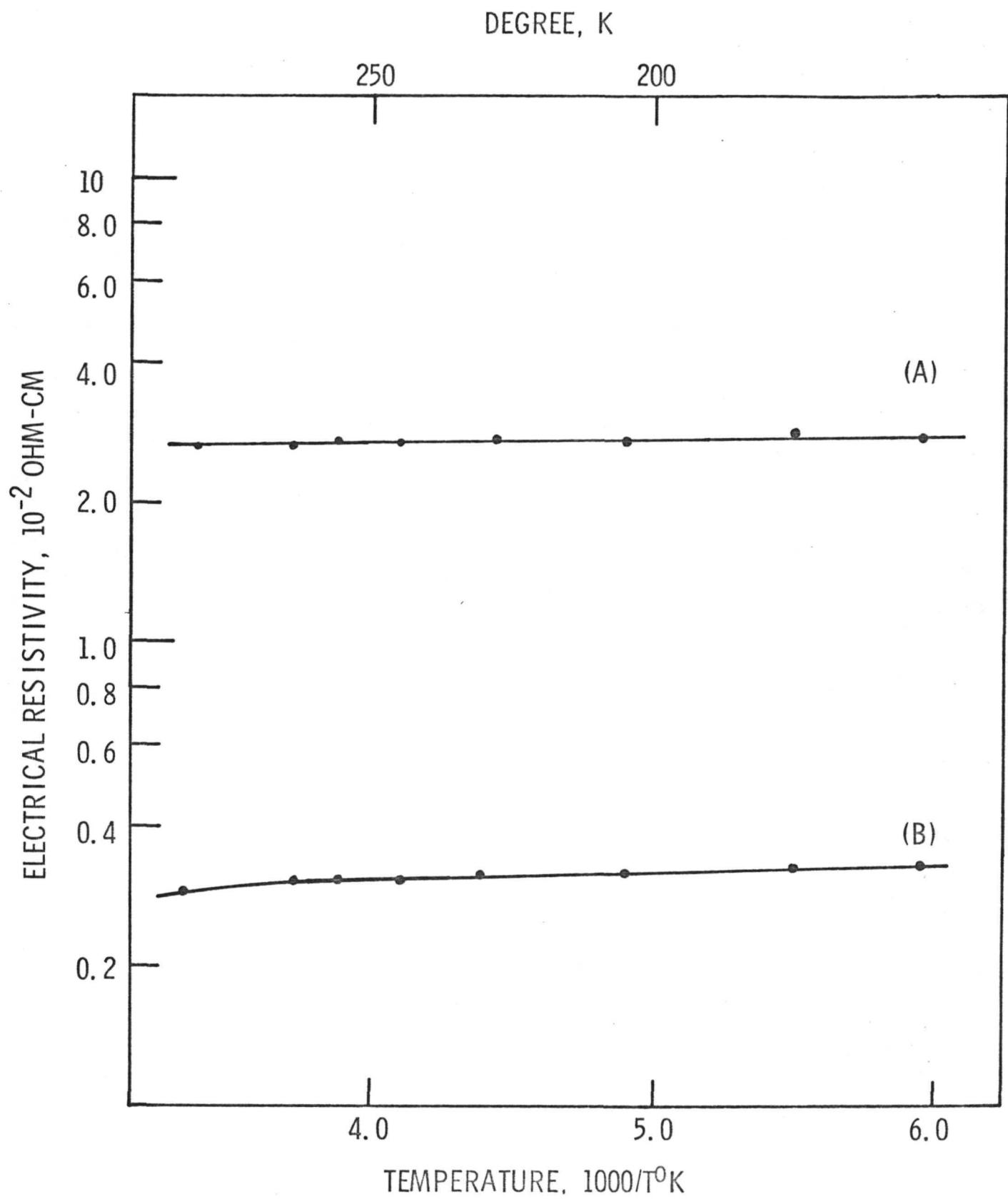


Fig. 3. Electrical resistivity of gallium nitride crystals grown in the alumina boat (A) and on the wall of the silica tube (B) by the sublimation technique.

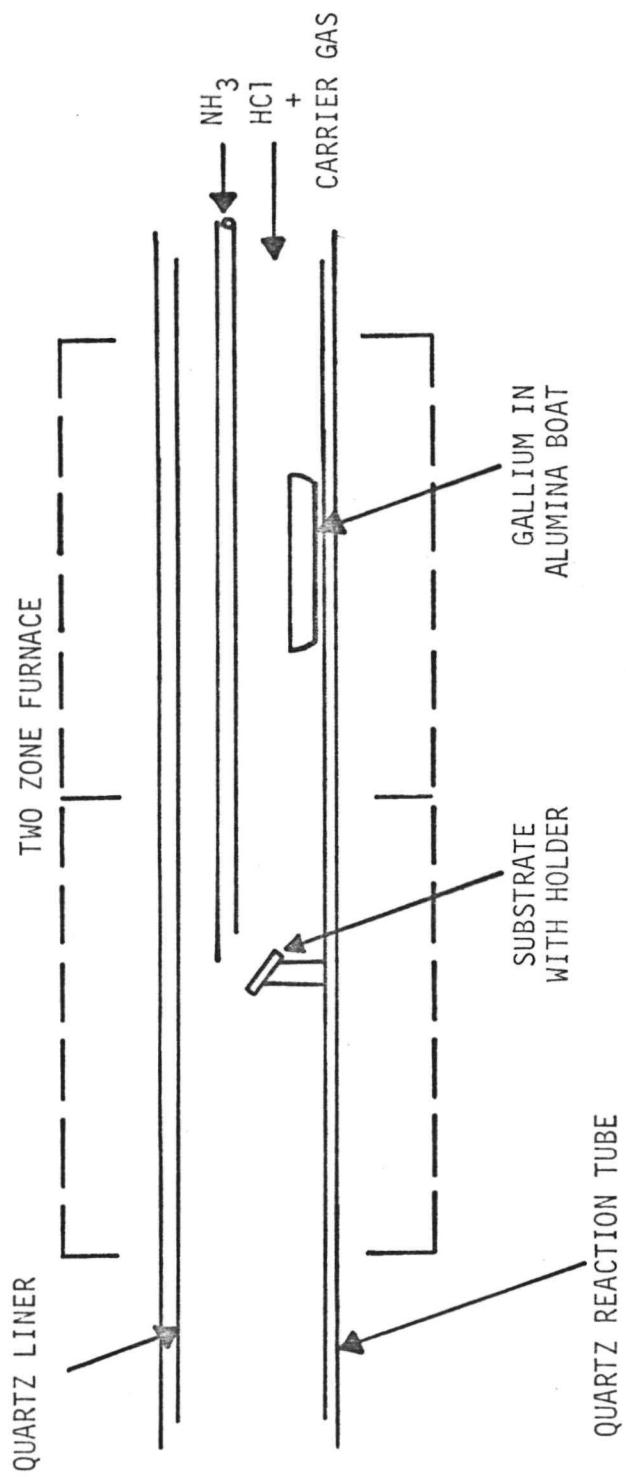


Fig. 4. Schematic of the apparatus for the growth of bulk gallium nitride crystals by the ammonolysis of gallium monochloride.

with main faces of (1102) orientation were used as substrates. The geometric relationship between the substrate and the ammonia outlet was found to be the most critical parameter in this process. Because of the strong reactivity of ammonia toward gallium monochloride, the ammonia outlet should be very close to the substrate surface to minimize the volume reaction and to achieve the maximum yield. To obtain a uniform deposit, the substrate was oriented about 30° from the horizontal. Both hydrogen and helium were used as the carrier gas. Hydrogen was purified by diffusion through palladium-silver alloy, and helium was purified by passing through a liquid nitrogen trap and a fused silica tube containing copper turnings at 550°C. When helium was used as the carrier gas, the typical flow rates of ammonia, hydrogen chloride, and helium were 1000, 20, and 2000 ml/min, respectively. The gallium source was maintained at 900°C, and the temperature of the substrate was 1050°C. The reaction time was usually six hours, and the grown material was usually 2-5 mm thick weighing up to 4 g. The yield of the deposition process was about 15% on the basis of gallium consumption. Deposition on the basal plane of sapphire substrates did not yield crystals of comparable weight or thickness.

After the deposition process, the sapphire substrate may be removed by lapping with silicon carbide abrasive. When the resulting gallium nitride crystal was used as a substrate for the growth process, it was first mechanically polished with alumina abrasive and etched in-situ with a hydrogen-hydrogen chloride mixture at 850°C.

Figure 5 shows two typical gallium nitride crystals grown on a sapphire substrate of (1102) orientation and a gallium nitride substrate. Figure 6 shows two polished gallium nitride crystals cut from the larger crystals, and the upper crystal was etched in a 40% sodium hydroxide

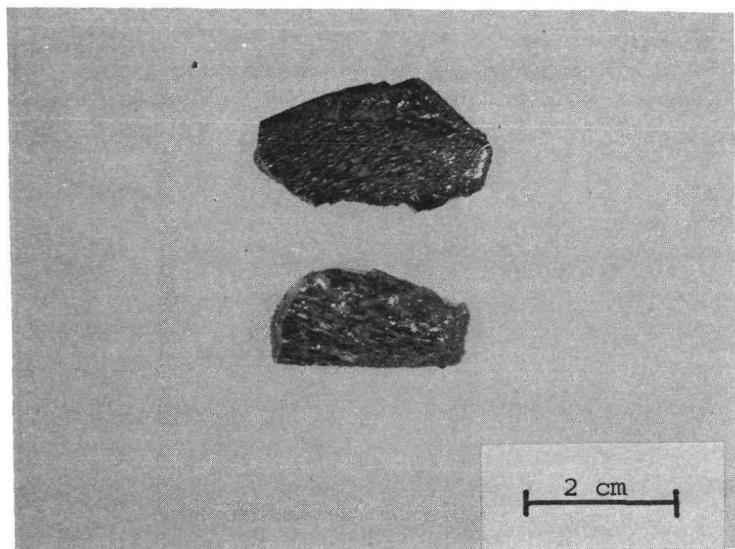


Fig. 5 Gallium nitride crystals obtained by the ammonolysis of gallium monochloride. The upper crystal was grown on a sapphire substrate of (1102) orientation, and the lower crystal was grown on a gallium nitride substrate.

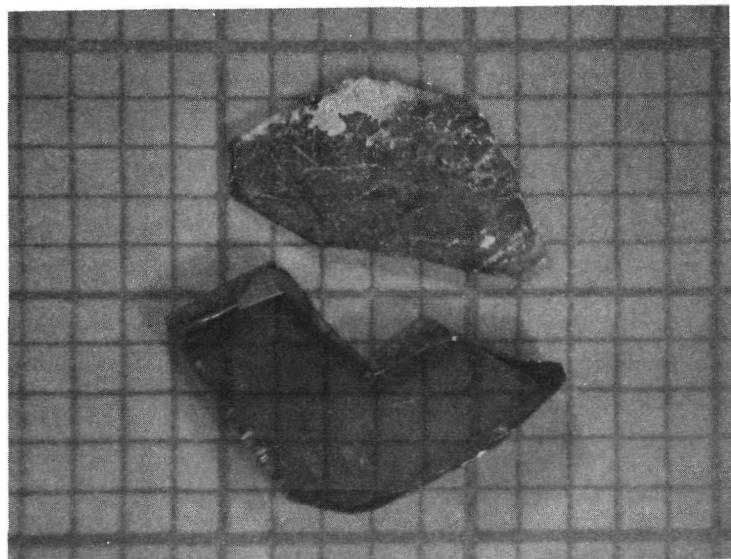


Fig. 6 Two gallium nitride crystals cut from larger crystals. The upper one was etched in a 40% sodium hydroxide solution at 100°C for 30 min. Scale divisions are millimeters.

solution at 100°C for 30 min. The etch figures in the crystal are shown at higher magnifications in Fig. 7, taken by both transmitted and reflected light.

Figure 8 shows the angle-lapped and chemically-etched surface of a gallium nitride crystal deposited on a gallium nitride substrate where the substrate was grown on sapphire. As expected, the grown crystal has much better structural perfection than the substrate as indicated by the relatively heavy attack of the substrate by the sodium hydroxide solution.

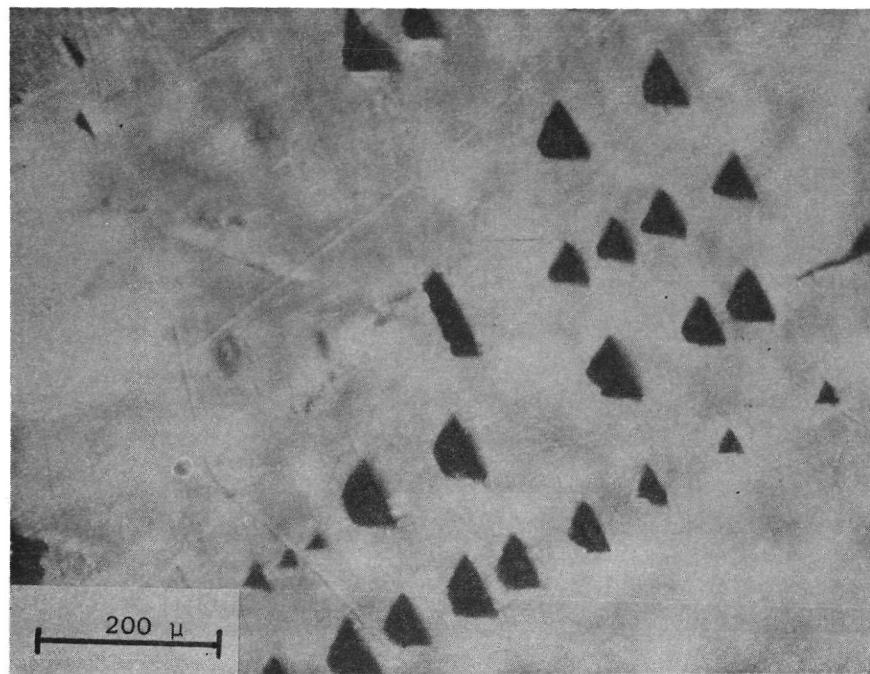
The electrical properties of the bulk gallium nitride crystals separated from sapphire substrates were measured at 77° and 300°K by the van der Pauw technique.⁽¹³⁾ At room temperature, the bulk crystals had an electron concentration of approximately 10^{19} cm^{-3} and carrier mobilities in the range of $100-160 \text{ cm}^2 \text{ v}^{-1} \text{ sec.}^{-1}$. The carrier concentration was essentially the same at 77°K; however, the mobilities decreased by about 25% due presumably to impurity scattering.

II.B. Epitaxial Growth of Gallium Nitride

Concurrent with the investigation of bulk gallium nitride crystals, the epitaxial growth of gallium nitride on various substrates by the ammonolysis of gallium monochloride was investigated. The most important parameters affecting the structural and electrical properties of epitaxial gallium nitride include the geometry of the deposition apparatus, the composition and flow rate of the reactants, and the substrate temperature.

The apparatus used for the epitaxial growth of gallium nitride is shown schematically in Fig. 9(a) and (b). Common to the two configurations is a fused silica reaction tube of 36 mm ID and 90 cm in length situated in a two-zone resistance-heated furnace. Both ends of the reaction tube are provided with standard taper joints and end caps. The end cap on the

(a)



(b)

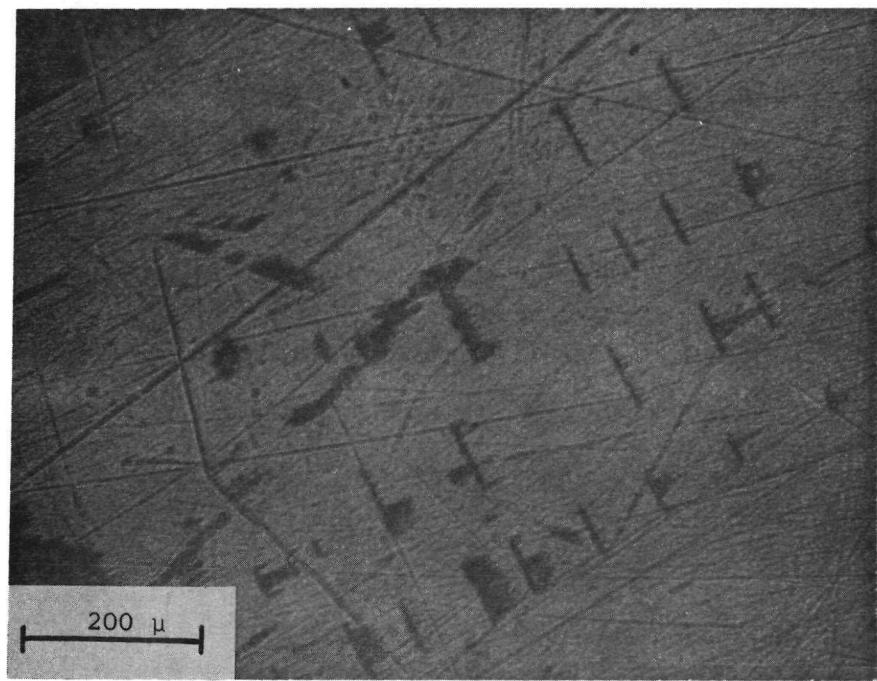


Fig. 7 Etch figures in the upper crystal in Fig. 6 by transmitted light (a) and by reflected light (b).

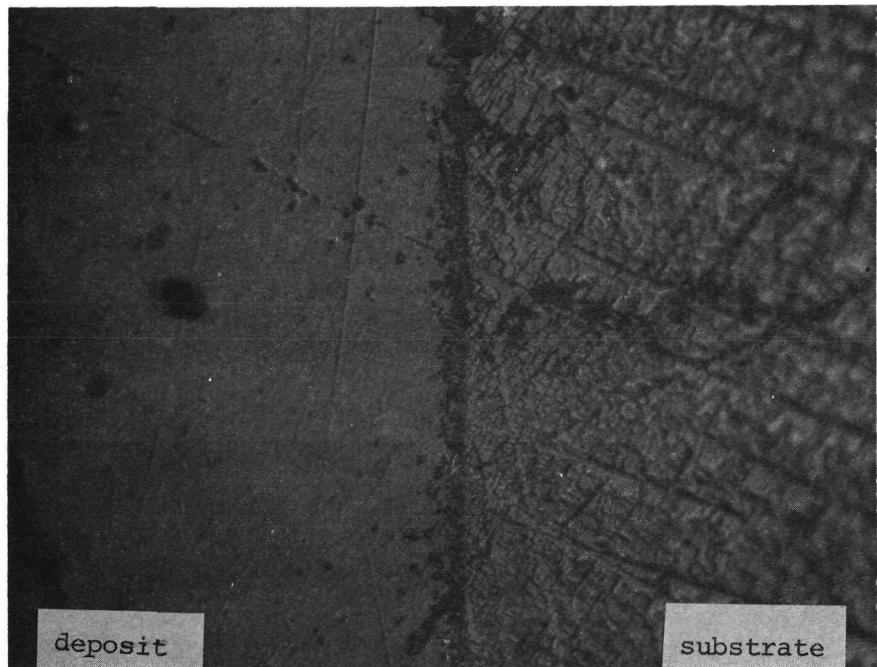


Fig. 8 The angle lapped and chemically etched surface of a gallium nitride crystal deposited on a gallium nitride substrate. Etchant: 40% sodium hydroxide solution at 100°C for 30 min.

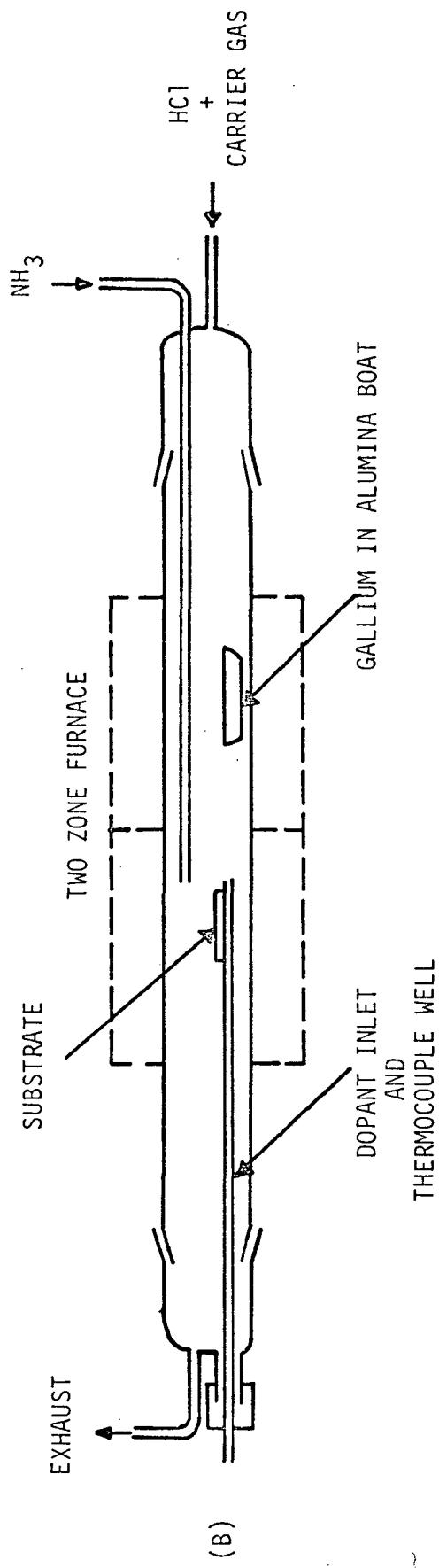
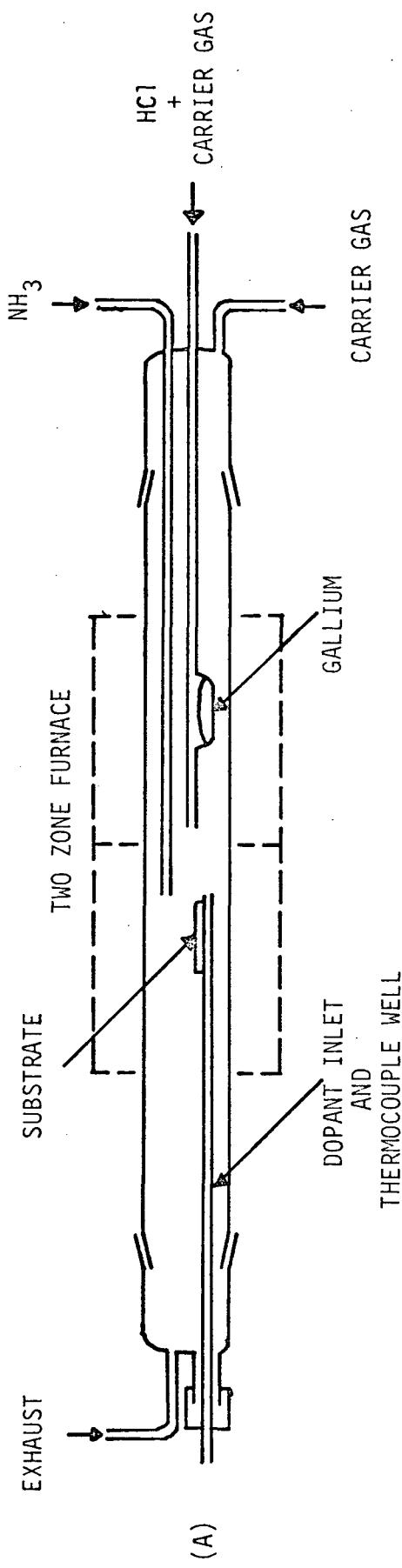


Fig. 9 The two configurations of apparatus used for epitaxial growth of gallium nitride.

gas inlet side has the necessary connections for introducing the gases and a sealed tube serving as a thermocouple well near the gallium boat. The end cap on the exhaust side of the reaction tube supports the substrate holder with a thermocouple well and has provisions for introducing a dopant. In one configuration, Fig. 9(a), the gallium source is a closed boat, and the gallium monochloride enters the gallium zone from a nozzle. In the other configuration, an open boat was used for the gallium and the gallium monochloride enters the reaction zone as a uniform flux. The second configuration, though less effective in utilizing the gallium source material, was used in most of the experiments because it was convenient and provided more uniform deposits.

Many geometric factors such as the diameter and shape of the ammonia outlet, the location and orientation of the substrate, and the spacing between the ammonia outlet and the substrate were investigated within these two basic configurations using the crystallinity, uniformity, and electrical properties of the grown layers as criteria. A series of experiments were carried out using various configurations of the ammonia outlet tube, such as a simple open tube of different sizes, a downward facing slot, and a funnel-shaped opening. The optimum configuration was determined to be a simple open tube of 8 x 10 mm. Various substrate locations and orientations were also investigated. A horizontal orientation was considered the best, and the optimum location was within 8 cm from the ammonia outlet. For each experiment, one substrate was located 3.5 cm from the ammonia outlet and a second substrate was about 2-3 cm further down. The front substrate always had a thicker deposit than the rear one. The vertical spacing between the substrate and the ammonia outlet was kept within 1 cm. The distance between the gallium boat and the ammonia outlet was about 10 cm, and this

spacing is not critical.

Other parameters, such as the nature of the substrate, the reactant composition and flow rate, and the substrate and gallium source temperatures, were considered to be more critical than many of the geometric factors. Initial experiments were carried out to investigate the use of silicon carbide and sapphire as substrates. Although the lattice match between gallium nitride and silicon carbide is considerably better than that between gallium nitride and sapphire, the large difference in the thermal expansion coefficient between gallium nitride and sapphire leads to the cracking of the deposited layer at thicknesses greater than about 5 μm . Subsequent experiments were carried out with sapphire and, in a few cases, gallium nitride substrates. Sapphire substrates with main faces of (0001) and (1102) orientations were used, and no significant difference in the properties of the grown layers was observed.

The use of hydrogen, helium, and nitrogen as carrier gases was studied; however, no conclusive results were obtained with nitrogen. Both hydrogen and helium could be used to obtain single-crystalline, epitaxial, light-colored layers. It was observed that the deposition rate and characteristics of gallium nitride depended on the ratio of flow rates of the carrier gas to ammonia and on the ratio of flow rates of ammonia to hydrogen chloride. For the configuration shown in Fig. 9(b), the optimum flow rates of helium and ammonia are 2 and 1 l/min , respectively, and those of hydrogen and ammonia were 1 and 3 l/min , respectively. For either carrier gas, there was a range of hydrogen chloride flow rates which could be used to obtain uniform deposits. A minimum flow rate of 3 ml/min with helium as the carrier gas and 5 ml/min with hydrogen as the carrier gas was required to obtain uniform nucleation on the substrate. At lower flow rates, isolated crystallites tended to form on the substrate. Excessive flow rates of hydrogen chloride,

above about 10 ml/min in helium and 20 ml/min in hydrogen, yielded polycrystalline deposits thicker than 100 μm after one hour of deposition. Single crystalline layers were obtained with growth rates in the range of 10 to 60 $\mu\text{m}/\text{hr}$ by controlling the flow rate of hydrogen chloride.

The temperatures of the gallium source and the substrate are also of importance. Varying the gallium source temperature near 900°C did not influence the epitaxial growth process, and the substrate temperature was a very critical parameter. When helium was used as a carrier gas, a deposition temperature of 1050°C was found to be optimum, and at temperatures below 1000°C, the grown layer was always dark and of low resistivity. With hydrogen as a carrier gas, a growth temperature near 950°C was normally used, and epitaxial growth was achieved at temperatures as low as 875°C.

The grown layers were characterized by optical microscopy, x-ray diffraction, and Hall measurements. The crystallinity of the layers could usually be determined by optical examination, and x-ray techniques were used to verify the optical observations. The best layers grown on the basal plane of sapphire were essentially colorless and showed no structural features under an optical microscope. In very thin layers, hexagonal structure was sometimes visible near the periphery of the substrate. Layers grown on sapphire substrates of (1102) orientation had wave-like features on the surface and were also shown to be single crystalline by the Laue method.

The electrical properties of epitaxial gallium nitride layers were determined from four-point probe, thermoelectric, and Hall measurements. The resistivity values obtained from the four-point probe technique were in good agreement with those from the Hall data, and the four-point probe technique was used for routine resistivity measurements. All epitaxial layers were n-type, and the lowest carrier concentrations were about 10^{19} cm^{-3} .

Hall mobilities up to $80 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ were measured at room temperature, and the typical room temperature resistivities were about $3 \times 10^{-3} \text{ ohm-cm}$. These values were obtained by using both helium and hydrogen as the carrier gas. Efforts were made to dope the epitaxial gallium nitride layers with zinc; however, the electrical properties of the doped layers have not been measured.

III. Conclusions

(1) Epitaxial and single-crystalline gallium nitride layers have been grown on sapphire substrates with main faces of (0001) and (1102) orientations. The grown layers are n-type with electron concentrations in the range $1-3 \times 10^{19} \text{ cm}^{-3}$ and Hall mobilities in the range of 50-100 $\text{cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at room temperature.

(2) The use of sapphire substrates is not the best approach for the preparation of gallium nitride device structures because of the differences in lattice parameters and thermal expansion coefficients between gallium nitride and sapphire.

(3) Bulk crystals of gallium nitride have been grown from the vapor phase by sublimation, ammonolysis of gallium suboxide, and ammonolysis of gallium monochloride. The ammonolysis of gallium monochloride has produced large gallium nitride crystals up to $2.5 \times 1.0 \times 0.5 \text{ cm}$ in size, heretofore unknown. These crystals with an electron concentration of 10^{19} cm^{-3} and Hall mobilities of $100-160 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$ at room temperature are best suited as substrates for the preparation of epitaxial gallium nitride device structures.

IV. References

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16. Abstract The growth of bulk gallium nitride crystals has been achieved by the ammonolysis of gallium monochloride. Gallium nitride single crystals up to $2.5 \times 1.0 \times 0.5$ cm in size have been produced. The crystals are suitable as substrates for the epitaxial growth of gallium nitride. The epitaxial growth of gallium nitride on sapphire substrates with main faces of (0001) and (1T02) orientations has been achieved by the ammonolysis of gallium monochloride in a gas flow system. The grown layers had electron concentrations in the range of $1-3 \times 10^{19}$ cm ⁻³ and Hall mobilities in the range of $50-100$ cm ² v ⁻¹ sec ⁻¹ at room temperature.			
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